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Produced Water Treatment Using Ultrafiltration and Nanofiltration Membranes

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Abstract

The application of ultrafiltration (UF) and nanofiltration (NF) processes in the handling of raw produced water have been investigated in the present study. Experiments of both ultrafiltration and nanofiltration processes are performed in a laboratory unit, which is operated in a cross-flow pattern. Various types of hollow fiber membranes were utilized in this study such as poly vinyl chloride (PVC) UF membrane, two different polyether sulfone (PES) NF membranes, and poly phenyl sulfone PPSU NF membrane. It was found that the turbidity of the treated water is higher than 95 % by using UF and NF membranes. The chemical oxygen demand COD (160 mg/l) and Oil content (26.8 mg/l) were found after treatment according to the allowable limits set by means of world health organization WHO water quality standards. The final composition of SO_4^{-2} (110 mg/l) and NO_3 (48.4 mg/l) components within the produced water after treatment were agreed with the permissible limits of WHO, whereas Cl^{-1} (8900 mg/l) component is not in the allowable limits. Finally by the use of PVC, PES and PPSU hollow fiber membranes; this method is seen to be not sufficient to remove the salinity of the produced water.

Keywords: *Ultrafiltration membrane, Nanofiltration membrane, Oily wastewater, Produced water, Desalination.*

1. Introduction

In fact the importance of the use of both nanofiltration (NF) and ultrafiltration (UF) membranes for separation processes are hastily growing and extending to include vast field of industrial applications. Among the industrial application of UF and NF, the treatment of produced water is dominated to remove the oil, suspended solid, and organic compounds [1,2].

Produced water includes a huge amount of oil hydrocarbons, salts, and dangerous matters, which is considered a toxic materials to environment. Therefore, it is important to treat this water before disposal and either reuse it for irrigation, or re-inject to the well.

Over the years, many researchers have been performed on the treatment of produced water that association within oilfields. Cakmakci et al. [2] had investigated the pretreatment of produced water in the alternative reverse osmosis (RO) and NF membranes. The authors were found a suitable handling combination. In addition, microfiltration (MF) and UF were employed as a pretreatment of produced water, while RO and NF were utilized to decrease the salt content as a final treatment.

With reference to the conventional separation methods that are usually utilized in the treatment of produced water, the UF seems to be one of the most successful method owing to its high efficiency of oil extraction, smaller space requirements, lower energy costs, and no necessity to use the other chemical additives during the treatment [3].

Bilstad and Espedal [4] reported the treatment of produced water of North Sea oilfield by using ultrafiltration (UF) and microfiltration (MF) membranes. It was found that the hydrocarbon content decreased from 50 mg/l to 2 mg/l from and the removal efficiency of UF membrane was 96%. Moreover, heavy metals, for instance, Zn and Cu were diminished by about 95%.

Furthermore, RO process and incorporated membrane pretreatment such as ultrafiltration (UF), and nanofiltration (NF) processes are nowadays seen to be the significate techniques for the treatment produced water application [5,6]. Moreover, Xu and co-authors [7] studied the treating of produced water created from sand-stone aquifers by using nanofiltration (NF) and reverse osmosis (RO) membranes operated at very low transmembrane pressure. They are reported that the treated water can be used for irrigation and potable water. Also, Ashaghi et al. [8] used UF and NF ceramic membranes (membrane prepared from new materials) for the treatment of produced water. Mondal and Wickramasinghe [9] used two NF and one RO membrane for handling of various produced waters. They found that NF membrane was more applicable process for treatment of produced water according to the nature of the produced water and the water quality requirements.

In this work, the application of either ultrafiltration (UF) or nanofiltration (NF) process was fundamentally studied in the treating of the raw produced water. A variety of hollow fiber membranes types were employed (i.e. PVC UF membrane, two different PES NF membranes, and PPSU NF membrane) in order to measure the Turbidity, TDS, COD, Oil, NO_3, SO_4 and Cl^{-1} removal efficiency of different membrane processes and focus on combined UF and NF techniques to enhance outflowing quality of the water.

2. Experimental Work

2.1 Experimental System and Procedure

Figure 1 shows a graphical diagram of the wastewater treatment system used in this study. The feed wastewater is pumped from the feed tank of UF via a diaphragm pump into the hollow fiber membrane module. The effective length of the hollow fiber module is 20 cm and the number of used hollow fiber is 8 with approximately 12 cm^2 effective area. The feed temperature is fixed at 35ºC. The ultrafiltration membranes were prepared from Poly vinyl chloride (PVC), whereas the nanofiltration membranes were prepared from polyether sulfone (PES) and Poly phenyl sulfone (PPSU).

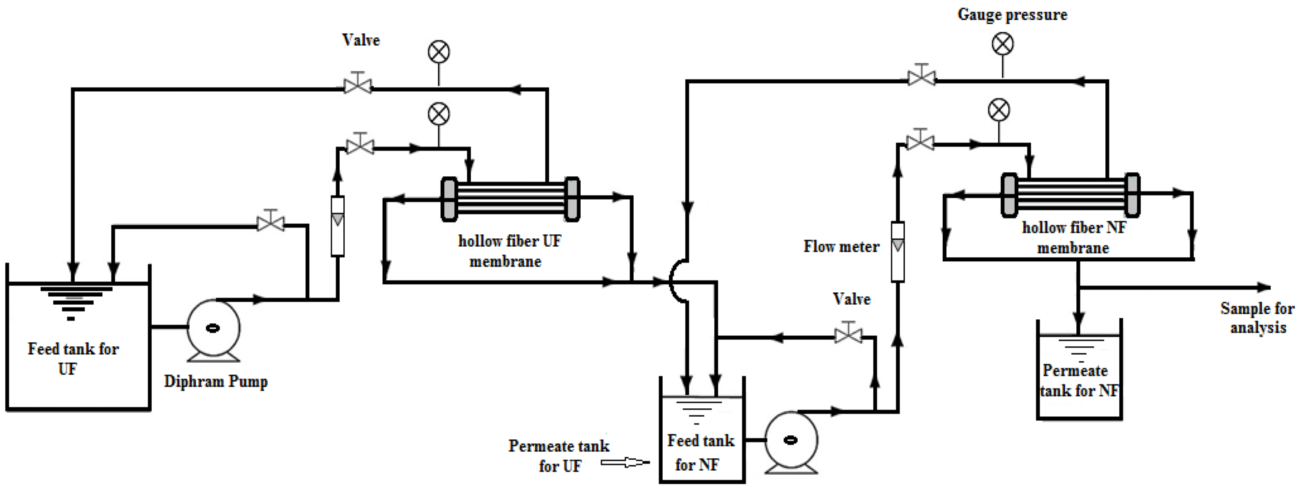
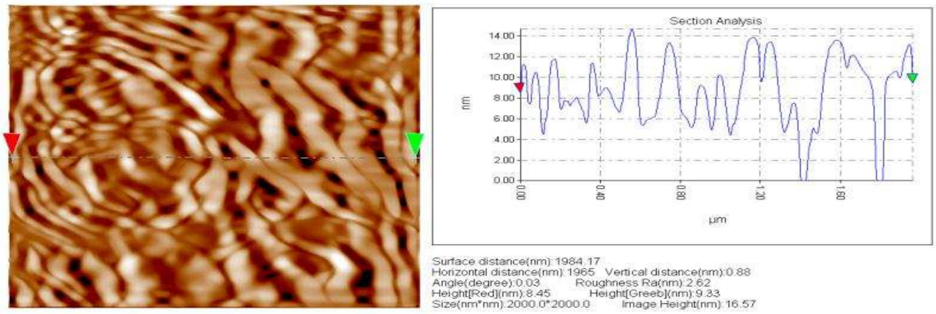


Fig. 1. Schematic diagram of the raw produced water treatment system.

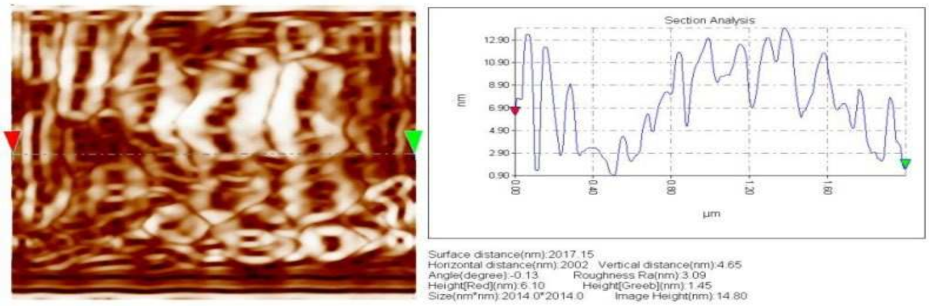
The specifications of the ultrafiltration and nanofiltartion membranes are illustrated in Table 1 and also demonstrated in Figure 2.

Table 1,
Properties of the prepared UF and NF hollow fiber membranes.

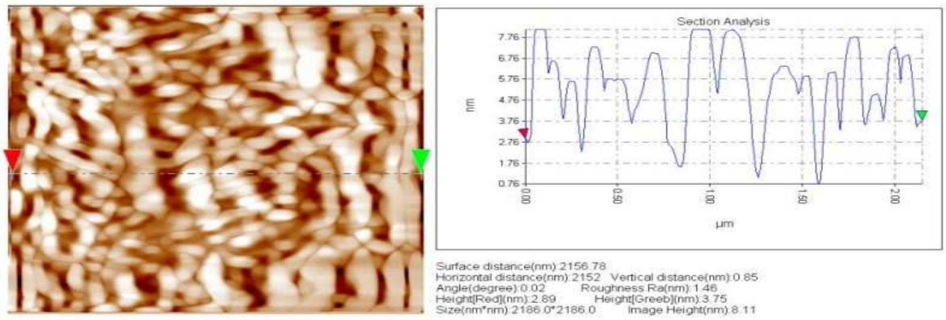
Membrane Code	Material and composition	Porosity	Mean pore size nm	Outer dia. mm	Inner dia. mm	Length of fiber cm
UF	PVC\DMAC (16:84)	77%	120	1.2	1.0	30
NF1	PES/DMAC (29:71) Extrusion pressure is (1.5 bar)	56%	42.95			20
NF2	PES/DMAC (29:71) Extrusion pressure is (1.0 bar)	62%	53.52			20
NF3	(PPSU/NMP) (29:71)	49%	40.3			20



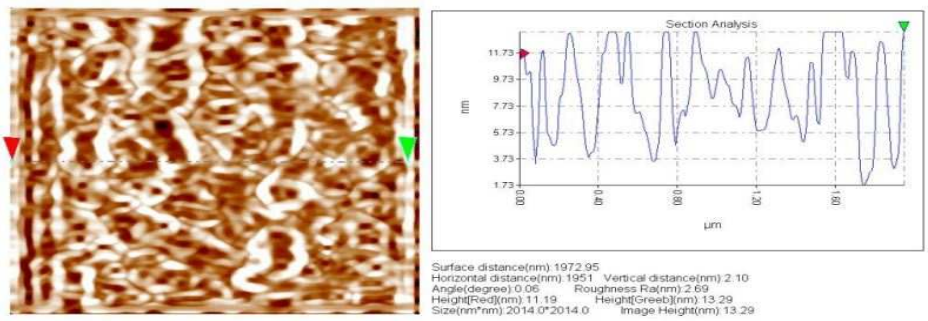
UF



NF1



NF2



NF3

Fig. 2. Two dimensions AFM images of the UF and NF membranes.

The experiments were carried out in a batch circulation process where the concentrated solution is returned back to the feed tank, while the permeate stream is flowed to the permeate tank of UF process (Feed tank for NF). Ultrafiltration membrane (UF) is utilized mainly to the elimination of high molecular-weight substances, total suspended solids (TSS), oil content, and either organic or inorganic polymeric molecules. This means that the hollow fiber (UF) membrane might be employed as a pre-treatment for hollow fiber NF membranes. Besides, organics and ions that possess low molecular-weights like sodium, calcium, magnesium chloride, and sulfates as well as the heavy metals have been removed through the hollow fiber UF and NF membranes. The operating pressure of NF membranes is 6 bar and the trans-membrane pressures were determined from the difference between the pressures within the concentrate and permeate streams. Accordingly, the solutions from the feed tank and the permeate flow were sampled for analysis. For each sample, both the removal efficiency (rejection) and the volume flux were measured at the steady state, which are established by approximately 30 min. The solute removal efficiency (rejection) (R%) was defined as follows:

$$R(\%) = [(C_f - C_p)/C_f] \times 100 \quad \text{…. (1)}$$

Where; C_f and C_p are the concentrations of the feed and the permeate flow, respectively. Indeed, the concentration of both Pb and Cd ions within the feed stream and permeate streams were measured using Atomic Absorption (spectrometer), PERKIN ELMER 5000.

2.2. Analytical Methods

2.2.1. Determinations of COD and Turbidity

The Chemical Oxygen Demand (COD) of the wastewater can usually be determined via spectrophotometer method with Hach DR 2800 system and consistent with 5220 American Public Health Association (APHA) methods. Likewise, the turbidity of the wastewater was carefully calculated by applying the turbidity meter (WTW TURB 550, Inolab).

2.2.2. Determination of Oil content (5520 APHA)

The quantity of associated oil with the wastewater was estimated next to the extraction from water due to intimate contact by means of an extracting solvent (CCl_4). Subsequent to the removal route in a Soxhlet apparatus with solvent, the remaining residue from the evaporated solvent is weighed in order to discover both oil and grease content. In fact, the volatilized compounds around or less than 103°C seen to be misplaced as soon as the filter had been dehydrated.

A 500 ml of permeate sample was stored in a conical flask, and then both (2.5-3.5) ml of HCl acid and 15 ml of CCl_4 were correspondingly added. The mixture was agitated and followed by stirring, which is led to appear an oil layer in the bottom of the conical flask. The completed oil layer was simultaneously withdrawn out and kept inside a weighted flask. Consequently, the flask is placed within a water bath for heating and after that dried out in an oven for 120 minutes at 360°C. The oil content was then calculated by applying the following equation:

$$W_f + W_{ef} = W_O \quad \text{….(2)}$$

Where W_f is the weight of flask with oil layer, W_{ef} is weight of empty flask and W_O is amount of Oil content.

3. Results and Discussion

It is well known that the wastewater needs to be pre-treated using Ultrafiltration and/or Microfiltration prior to the final treatment process by the use of Nanofiltration (NF) or Reverse Osmosis (RO) units with the aim of removing every undesired components (i.e., suspended materials, emulsions, and colloidal materials), which have an influence on the performance of either NF or RO membrane. Because of the increase in the requirements for pure water due to the continuous enlargement of population and the evolution of sustenance concept in addition to the insufficiency of water resources, the water reuse and/or solving these environmental and economical problems is thus becoming much more important. For that reasons, it is essential to make treatment to the wastewater within the specification limits according to the WHO earlier than discharging as explained in Table 2.

Table 2,
Characteristics of raw produced water with WHO water quality standards.

Parameters	Units	Values	WHO
Turbidity	(NTU)	9.5	1-5
Conductivity	(µS/cm)	32600	500-2000
TDS	(mg/l)	15870	1200
PH		8.5	6.5-8.5
COD	(mg/l)	383	200
TOC	(mg/l)	112	200
Oil content	(mg/l)	98.8	10
TSS	(mg/l)	126	0-200
Mn	(mg/l)	0.11	
Fe	(mg/l)	Nil	0.3
Zn	(mg/l)	0.08	5
Pb	(mg/l)	0.04	0.01
Ni	(mg/l)	0.01	0.02
Cr	(mg/l)	0.02	0.05
Cu	(mg/l)	0.05	2
Cd	(mg/l)	0.01	0.003
Cl^-	(mg/l)	8900	200
SO_4^{-2}	(mg/l)	110	250
NO_3	(mg/l)	48.4	10-50

Figure 3 shows the turbidity removal efficiency of produced water by using various membrane separation processes. It can be seen that the turbidity of the produced water is decreased from 9.5 to 0.48 Nephelometric Turbidity Unit NTU by using PVC hollow fiber ultrafiltration membrane (i.e. 95% removal efficiency). Whereas, further diminishing can be observed in turbidity of the produced water using NF1, NF2, and NF3 membranes (i.e. 0.25, 0.23 and 0.15, respectively). It seems during this study that the use of PVC hollow fiber UF membranes or NF membranes makes the turbidity of the produced water within the allowable limits of the WHO as presented in Table 2. It is worth to mention here that the small quantity of water turbidity may be alleviated the appearance of fouling as a result of organic components within UF and NF membranes, which may accordingly be led to the enhancement of the membrane performance.

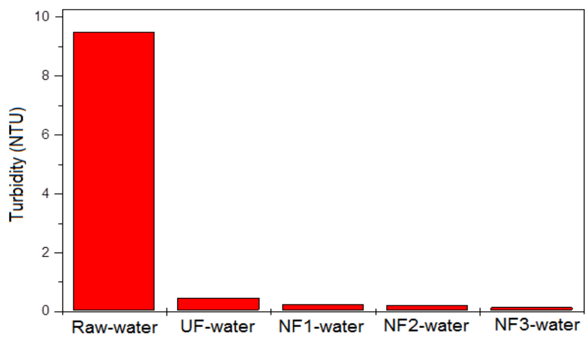


Fig. 3. Turbidity removal efficiency of different membrane processes.

Conductivity of water is an indicator to presence of inorganic dissolved solids such as either the negative ions of chloride, sulfate, phosphate, and nitrate anions or the positive ions of sodium, calcium, magnesium, aluminum, and iron cations. The conductivity of raw produced water is about 32600 (µS/cm), whereas the conductivity value of the WHO water quality standards should be 500-2000 (µS/cm) as scheduled in Table 2. Therefore it can be stated that the use of UF with three different NF hollow fiber membranes would be able to decrease the conductivity of water, and a minimum value of 10000 (µS/cm) could be obtained by applying the NF3 as shown in Figure 4.

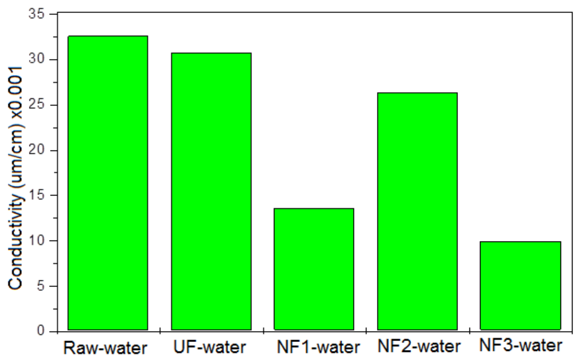


Fig. 4. Conductivity difference between various membrane processes.

The total dissolved solid (TDS) of the raw produced water is about 15870 (mg/l) and the standard magnitude value should be not exceed than 1200 (mg/l) as illustrated in Table 2, since a high TDS concentration means a high dissolved salts concentration.

Figure 5 establishes the TDS removal efficiency of different hollow fiber membrane processes. It can be seen that the higher removal efficiency is 6090 (mg/l) using NF3 hollow fiber membrane. It is worth to mention here that all the revealed values of TDS for the treated water are at concentrations upper than the acceptable irrigation or drinking water standards.

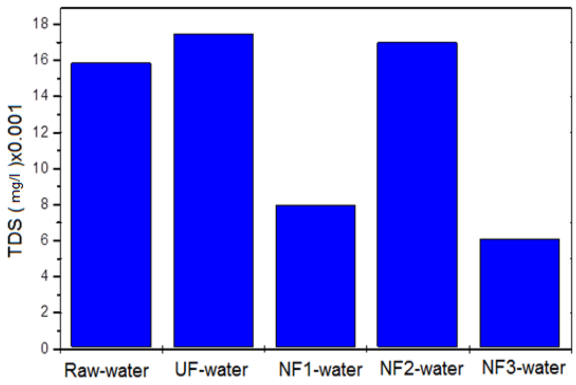


Fig. 5. TDS removal efficiency by using different membrane processes.

Figure 6 confirms the COD removal efficiency of produced water by using different hollow fiber membrane processes. It can be noticed that the COD of the raw produced water is decreased from 383 to 160 (mg/l) using PVC hollow fiber UF membrane and this magnitude value is in fact less than the permissible restrictions set by WHO water quality standards as exemplified in Table 2 and Table 3. With the purpose of reduction the COD value within the treated water by utilized UF hollow fiber membrane, three different NF membranes have been employed and the obtained value of COD by NF3 seems to be attained approximately 122 (mg/l).

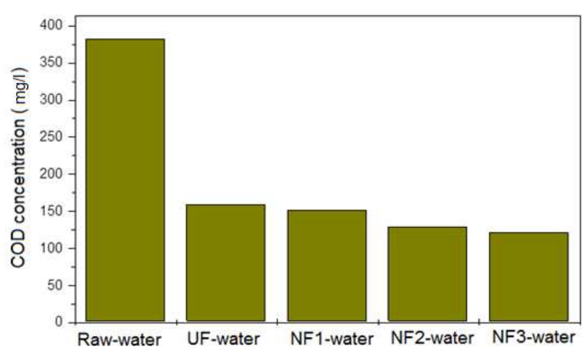


Fig. 6. COD removal efficiency of different membrane processes.

One of the potential sources of environmental pollution is the oil content. This was observed when the analysis was accomplished on the raw produced water, since the value of oil concentration is reached to 98.8 (mg/l) as given in Table 2. The results of analysis of a pre-filtration sample (i.e. permeate sample out from UF membrane) are detected that the oil concentration of produced water is within 26.8 (mg/l) as illustrated in Table 3. Whereas, the post-filtration concentration of oil by using three different NF membranes such as NF1, NF2 and NF3 are seen to be reduced to 1.4, 1.0 and 0.07, respectively as proved in Figure 7. These magnitude values of oil concentration in permeate sample of NF membranes are lower than the permissible limits according to the WHO water quality standards as given in Table 2.

Figure 8 shows the removal efficiency of Cl^{-1}, SO_4^{-2} and NO_3 components of the produced water after treatment using different membrane separation processes. It can be noticed that the Cl^{-1} component was decreased from 8900 mg/l within the raw produced water to 780, 690, and 646 mg/l subsequent to the use of NF1, NF2, and NF3 with achieved removal efficiencies of 21, 61, and 89%, respectively. These magnitude values of Cl^{-1} concentrations inside the permeate stream of three different NF membranes are still higher than the allowable limits of WHO water quality standards as earlier mentioned in Table 2. The sulfate ion (SO_4^{-2}) within the raw produced water seems to be 110 mg/l with removal efficiency of SO_4^{-2} using UF membrane of about 27%. However, using NF membranes (i.e. NF1, NF2, and NF3) results to the reduction of SO_4^{-2} ion within the permeate stream and hence increasing the removal efficiencies to become 46, 75, and 75% respectively.

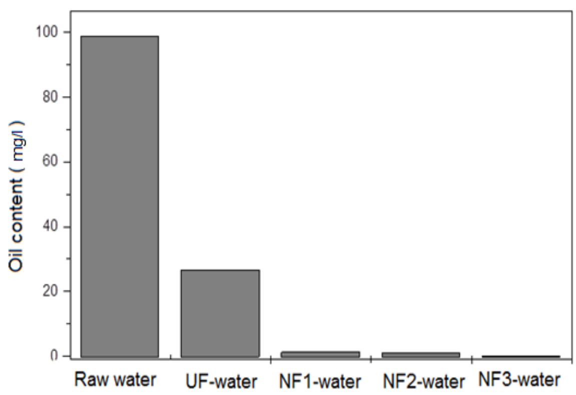


Fig. 7. Oil removal efficiency of different membrane processes.

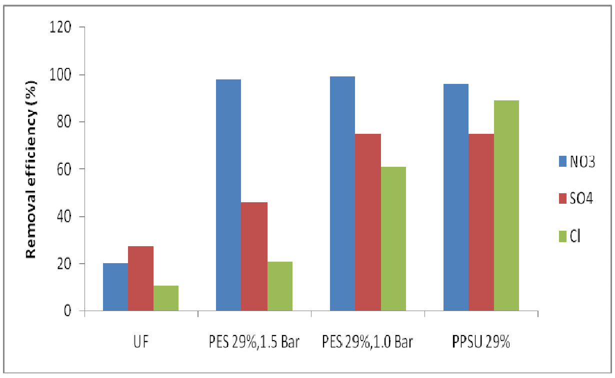


Fig. 8. Removal efficiency of NO_3, SO_4 and Cl^{-1} of the treated produced water.

Accordingly, all the obtained analysis for SO_4^{-2} within the post-treatment samples is seen to be complied with the licit limits specified by WHO water quality standards as confirmed in Table 2. Regarding to NO_3 removal efficiency, it can be observed in Figure 8 that the NO_3 elimination efficiency by applying UF membrane is 20%, but three different NF membranes have surprisingly been shown much high levels of NO_3 removal efficiency (i.e. 98, 99, and 96 % for NF1, NF2, and NF3, respectively). In addition, the analyzed permeate samples for NO_3 components are within the range of acceptable limits of WHO water quality standards as provided in Table 2.

During the last few years, consideration had been concentrated on the exclusion of heavy metal ions from the wastewater attributable to its toxicity and consequently its effect on the human health. For that reason and consistent with the environmental policy it is imperative to get rid of the entire heavy metals from the wastewater in different industries with the intention that the wastewater necessitates total control earlier than liberation into the environment [10].

Finally in Table 2, it can be recognized that all of the obtained heavy metals results either by pre-filtration (i.e. UF membrane) or post-filtration (i.e. NF membranes) are in reality within in the range of the allowed limits placed by WHO water quality standards excluding the Pb and Cd components. It is well known that both Pb and Cd ions are the most dangerous heavy metals owing to their stability inside the tissue of the human body. Hence, by using PVC hollow fiber UF membrane the removal efficiency of both Pb and Cd ions within the permeate stream is remained at 100% as offered in Table 3 [10].

Table 3,
Characteristics of produced water outflow from UF module.

Parameter	UF
Turbidity (NTU)	0.48
Conductivity (µS/cm)	30800
TDS (mg/l)	17500
pH	8.4
COD (mg/l)	160
TOC (mg/l)	5.1
Oil content (mg/l)	26.8
TSS (mg/l)	6
Mn (mg/l)	0.09
Fe (mg/l)	Nil
Zn (mg/l)	0.06
Pb (mg/l)	Nil
Ni (mg/l)	Nil
Cd	Nil
Cr	Nil

4. Conclusions

New hollow fiber membranes of different separation processes were utilized for the treatment of raw produced water with the aim of reuse it in other processes. By using UF and three different types of NF membranes, turbidity, COD, Oil content, TSS, all heavy metals - with the exception of neither Pb & Cd nor SO_4^{-2} & NO_3 - are perceived to be complied with the acceptable limits along with WHO water quality standards. The findings of this research detected that the permeate flow out from three hollow fiber NF membranes are still found to be elevated than the allowed restrictions of WHO water quality standards intended for conductivity, TDS and Cl^{-1}. It can be concluded that these types of membranes can be utilized to the removal of all contaminants except for conductivity, TDS and Cl^{-1}, thus it can be recommended to use such reverse osmosis membrane process to facilitate make the salinity of the treated water within the permissible limits of WHO water quality standards.

Acknowledgment

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معالجة الماء المنتج بأستخدام أغشية الترشيح الفائق والترشيح النانوي

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الخلاصة

في هذا العمل تم دراسة تطبيق عمليات الترشيح الفائق (UF) والترشيح النانوي (NF) في معالجة الماء المصاحب للنفط. تم اجراء تجارب مختبرية لكلتا عمليات الترشيح الفائق والترشيح النانوي بطريقة الجريان المتقاطع. تم أستخدام عدة انواع من أغشية الألياف المجوفة في هذه الدراسة مثل أغشية بولي فاينيل كلورايد PVC UF وغشائين مختلفين من بولي ايثر سلفون PES NF وغشاء بولي فينيل سلفون PPSU NF. وجد ان عكورة الماء المعالج هي اكثر من % 95 بأستخدام أغشية UF و NF. الاوكسجين الكيمياوي المطلوبCOD (١٦٠ ملغم/لتر) ومحتوى الزيوت (٢٦.٨ ملغم/لتر) وجدو بعد المعالجة وفقا الى الحدود المسموح بها حسب مواصفات الماء القياسية لمنظمة الصحة العالمية WHO. ان التركيز النهائي لمركبات SO_4^{-2} (١١٠ ملغم/لتر) و NO_3(٤٨.٤ ملغم/لتر) خلال الماء المصاحب للنفط بعد المعالجة قد توافقت مع الحدود المسموح بها من قبل منظمة الصحة العالمية WHO، في حين مركب Cl^{-1} (٨٩٠٠ ملغم/لتر) ليس من ضمن الحدود السموح بها. اخيرا بأستخدام اغشية الالياف المجوفة من نوع PVC، PES وPPSU فان هذه الطريقة غير كافية لازالة ملوحة المياه المنتجة.